

USE OF METALORGANIC COMPOUNDS IN THE PRODUCTION OF COATINGS BY THE PAMOCVD METHOD

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A b s t r a c t. A gaseous mixture composed of tetraisopropoxytitanium, nitrogen and hydrogen in the PACVD process, has been used to obtain Ti(NCO) layers of good performance properties, such as a high hardness and good resistance to corrosion and to frictional wear. The temperature of the process is 500°C. The paper describes a method which permits improving the properties of the Ti(NCO) type and composite nitrided + Ti(NCO) type layers by plasma nitriding treatment. The structure of the layers is described and their wear and corrosion resistance is determined. The results of SEM examinations, chemical composition, microhardness discussed. The nitrogen content can be increased by using pre-nitrided substrates and by subjecting the Ti(NCO) layers obtained to nitrogen plasma annealing. The next part of the paper presents the possibilities of obtaining chromium nitride layers from the gaseous mixture containing the chromium acetylacetonate vapours. The influence of process temperature on produced layers is discussed.

K e y w o r d s: surface layers, corrosion resistance, plasma nitriding.

INTRODUCTION

The Metalorganic Chemical Vapour Deposition (MOCVD) method, i.e., depositing coatings from a gaseous phase (enriched with metalorganic compounds) with the participation of a chemical reaction, is commonly used for producing compounds of III - V groups, such as GaAs or InP [1]. Slightly modified, the method has been applied to the production of gallium nitride - a material of high chemical resistance, with a very simple band gap whose width, at a temperature of 2 K, is 3.503eV (which corresponds to the emission of blue light wave) [2]. The MOCVD method, which uses a glow discharge for activating electrically the gaseous medium enriched with metalorganic compound vapours (donors of the metals intended to form the coating), known as the Plasma Assisted Metalorganic Chemical Vapour Deposition - PAMOCVD - is used at the Faculty of Materials Engineering, Warsaw University of Technology, for producing protective coatings, several micrometers thick, on tool- and constructional steels. The low-temperature

plasma, which is the source of the active particles involved in the formation of the coating, can be generated using a d.c. current or an a.c. current of a frequency elevated to about 100 kHz. The use of an impulse current permits shortening the deposition time and enables treating parts with small holes (below 3 mm in diameter).

The use of metallorganic compounds in depositing surface layers eliminates the necessity of using chloride atmospheres, common in CVD processes, and permits reducing the deposition temperature to below 500°C, which is crucial in the manufacture of tools of high-speed steels. The PAMOCVD method permits producing coatings of a variety of materials, such as TiN, Ti(C,N) [3], Ti(O,C,N) [4-8], polycrystalline diamond [9,10] and ZrO₂ [11].

It should be noted that, thanks to the low process temperature, the substrate materials on which the coatings are deposited may include, besides those used thus far, such materials as plastics [12,13] or ceramics [14], the use of which defines one of the perspective lines of the development of surface engineering.

The present study was concerned with the fabrication and properties of composite layers of the nitrated layer + Ti(NCO) type, produced with the participation of an organic titanium compound - isopropoxytitanium - subjected to annealing in a nitrogen plasma. Another experiment was devoted to the fabrication of chromium nitride coatings with the use of chromium acetylacetonate.

EXPERIMENTAL

The surface layers of the nitrated layer + Ti(NCO) were produced in a universal apparatus intended for glow discharge assisted treatments, which enabled the composition of the gaseous mixture to be modified during the process [5]. The surface layers were produced using a single-run process, i.e., immediately after completing the glow discharge assisted nitriding carried out in an N₂ + H₂ atmosphere, Ti(OC₃H₇)₄ vapours mixed with H₂ and N₂ were introduced into the reaction chamber, where, after modifying the process parameters such as the temperature which was adjusted to 520°C, the Ti(NCO) layers were deposited on an Armco iron substrate. The layers thus obtained were then annealed in nitrogen plasma at a temperature of 500°C.

The interest of many research centres in chromium nitride layers has been inspired by the specific properties of these layers, such as the high hardness and the good resistance to erosion, corrosion and frictional wear. These layers have mostly been produced using the PVD method. A new technology, consisting of a combination of galvanic chromium plating with glow discharge assisted nitriding, was developed at the Faculty of Materials Engineering, Warsaw University of Technology [15]. The present study presents the results of experiments on the

production of CrN by the PAMOCVD method with the use of chromium acetylacetonate - $(\text{CH}_3\text{COCH}_2\text{O})_3\text{Cr}$. Hydrogen and nitrogen were passed through the reaction chamber at a rate of $10 \text{ dm}^3/\text{h}$ each. The pressure in the chamber was 4 hPa. The substrate was Armco iron. The individual processes differed in the way in which the metalorganic compound was fed. At the first stage, a saturated solution of the compound in the acetic acid was used, dosed in a gravimetric way. The feeding time was 3h and the flow rate was $3\text{cm}^3/\text{h}$. The processes were carried out at temperatures of 400, 500, 600 and 700°C . The layers thus obtained however contained an excessive amount of carbon (soot was observed on the layer surfaces, especially in the layers produced at the higher temperatures). For this reason, we decided to deliver the chromium acetylacetonate directly to the reaction chamber. The compound was placed in a feeder heated by means of a heating jacket. The acetylacetonate vapours were swept by the hydrogen and nitrogen into the reaction chamber of the furnace. The processes were conducted at temperatures of 500, 600, 700 and 800°C , and the compound feeding time was 1h.

The examinations of the layers included: metallographical examinations, microhardness measurement, X-ray diffractometry, scanning electron microscopy, and determination of the chemical composition by the GDOS method. In addition to these examinations, we also determined the corrosion resistance (by the potentiodynamic method performed in a 0.5 M NaCl solution) and the frictional wear resistance (the 3 rollers + taper method) [16].

RESULTS

Ti(NCO) Layer

The Ti(NCO) layer ($8 \mu\text{m}$ thick) deposited on Armco iron appears to have a microhardness of about 1550 HV 0.05. The microhardness of an identical layer deposited on a pre-nitrided substrate is 1850 HV 0.05, whereas in the composite layer, final annealing increases the hardness to 1980 HV0.05. A GDOS analysis of the chemical composition of the layer shows that, in a layer subjected to prenitriding and then final nitriding, the nitrogen content has increased whereas the oxygen content has decreased. The results of these examinations are shown in Fig. 1.

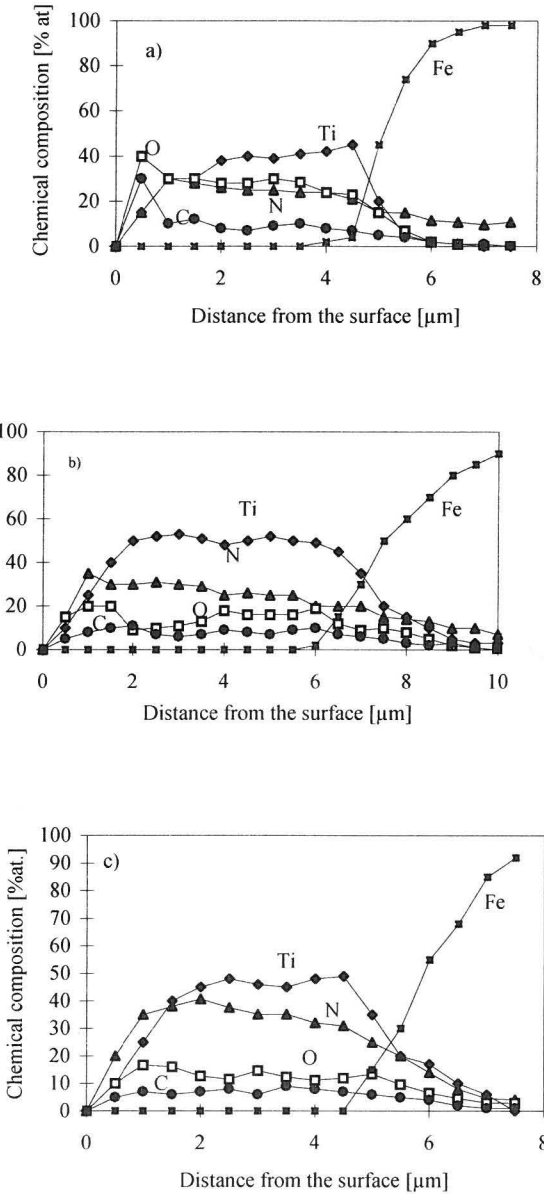


Fig.1. Chemical composition of a Ti(NCO) layer (a), a composite layer of the nitrated layer + Ti(NCO) type (b), and the composite layer subjected to final annealing in nitrogen plasma (c).

The results of examination of the surface microhardness are fully consistent with the results of the examination of the frictional wear resistance. It can be seen unequivocally that the best frictional wear resistance is shown by the layer produced on a pre-nitrided substrate that was then subjected to final glow discharge assisted nitriding (Fig.2).

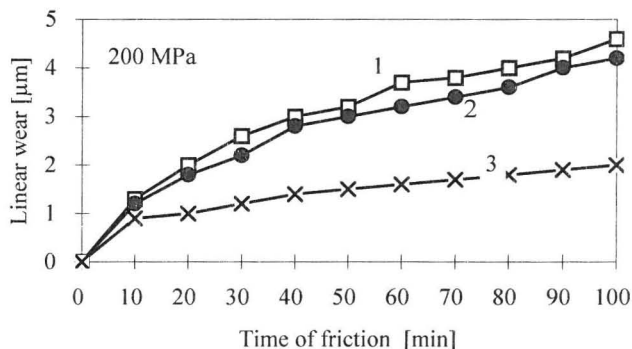


Fig.2. Plots of the frictional wear resistance of a Ti(NCO) layer (1), a composite layer of the nitride + Ti(NCO) type (2) and the composite layer subjected to final nitriding (3) as a function of the friction time under a unit load of 200 MPa.

Also the post-nitrided composite layer of the nitrided + Ti(NCO) type has the best resistance to corrosion. This can be seen in Fig.3. The corrosion resistance increases with increasing crystallite size. The pre- and post-nitriding make the layer structure more finegrained.

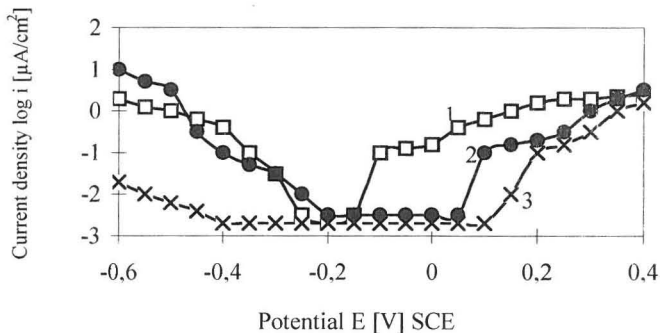


Fig.3. Plots of the corrosion resistance of a Ti(NCO) layer (1), a nitrided + Ti(NCO) type layer (2), and the composite layer subjected to final nitriding (3).

CrN Layer

The process with the participation of the solution of chromium acetylacetonate in acetic acid carried out at temperatures of 600 and 700°C only results in the Armco iron samples being carbonised. This can be attributed to the fact that the solvent contained 40% of carbon. To obviate this undesired effect, we changed the method of feeding the metallorganic compound. In the next trials, the vapours of this compound were mixed with nitrogen and hydrogen and then delivered to the reaction chamber. An analysis of the diffractograms of the layers thus obtained shows that, at a temperature of 500°C, it is the nitriding process which predominates - the phases identified in the layers were Fe_4N and Fe_3N . The CrN phase appears, together with the Fe_4N phase - which means that the nitriding process continues to proceed, when the temperature is increased to 600°C. The further increase in the process temperature to 700°C increases the amount of the CrN phase formed in the layer (increased microhardness). Under these conditions, too, the nitriding process continues to run (Fe_4N precipitates are present). At 800°C, the sample surface is covered with a soot layer. Figures 4a and b show the results of EDS examinations of the chemical composition of the layer surface in the samples treated at 600 and 700°C.

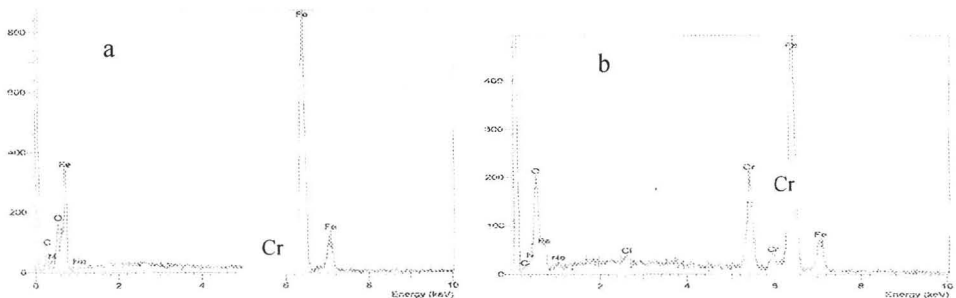


Fig.4. Chemical composition of the layers formed at a temperature of a) 600°C and b) 700°C (EDS results).

We can see that an increase in the temperature results in an increase of the amount of chromium present in the layer. This is consistent with the results of the phase examinations by the X-ray diffraction method. In view of the fact that the gaseous mixture delivered to the sample surface contains so many constituents, namely, chromium, carbon and oxygen from the metalorganic compound, and also nitrogen and hydrogen which are the main components of the gaseous atmosphere, the formation process of the surface layer is very complex, and the layer composition strongly depends on the process temperature. At the lower temperatures (about 500°C), the dominant process is the process of substrate

nitriding. An increase of the temperature to 600 and 700°C promotes the formation of a composite layer, i.e., a nitrided layer that possesses a CrN surface zone (identified by X-ray diffraction). A further temperature increase to 800°C results in the sample becoming carbonised; in effect, the surface microhardness decreases, and the sample surface is covered with soot. Fig.5. shows the boundary between the zones, exposed and not exposed to the action of corrosive surroundings, in the layer formed at 700°C (that showing the best corrosion resistance).

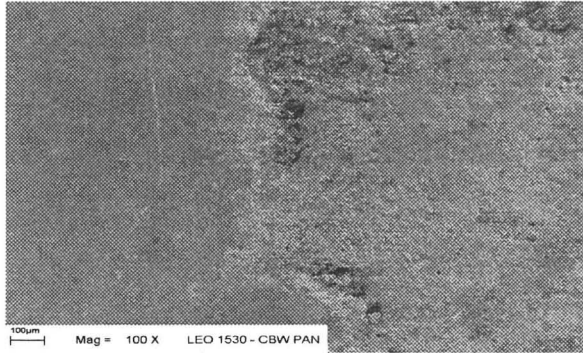


Fig.5. The boundary between the exposed and non-exposed portions of the surface in a layer produced at a temperature of 700°C.

The SEM photograph shows a well marked difference in topography between the surfaces exposed and non-exposed to corrosive surroundings. Although the surface layer seems to be smooth, it appears that it possesses cracks and is contaminated with carbon and oxygen. Nevertheless, its corrosion resistance has been increased (Fig.6), and the results of our experiments suggest that, by optimising the process parameters, it is possible to produce a solid chromium nitride layer.

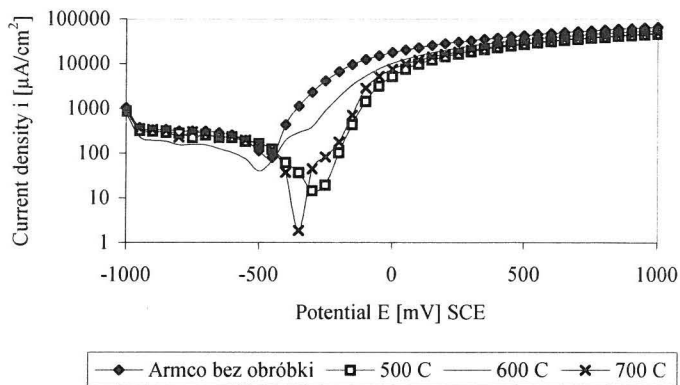


Fig.6. Curves representing the corrosion resistance of the layers produced at various process temperatures, compared to this obtained for an untreated substrate.

CONCLUSIONS

- By using the gaseous mixture of tetraisopropoxytitanium hydrogen and nitrogen in the PACVD process, we can produce a surface layer composed of titanium oxycarbonitride. Pre-nitriding of the substrate and the final annealing in nitrogen plasma atmosphere increase the nitrogen content of the Ti(NCO) layer and decrease its oxygen content; as a result, the surface hardness and the frictional wear resistance are increased. These treatments make the Ti(NCO) layer more finegrained and, in addition, increase its corrosion resistance.
- The PAMOCVD process in which chromium acetylacetonate is dissolved in acidic acid only results in the layer becoming carbonised. The PAMOCVD process carried out with the participation of chromium acetylacetonate vapours mixed with nitrogen and hydrogen produces composite layers of the CrN + (Fe₄N + Fe₃N) + diffusion zone type. An increase of the process temperature to 700°C facilitates the formation of the chromium nitride surface layers.

The present study was performed within the framework of the research project No PBZ-KBN-15/T09/99 sponsored by the State Committee For Scientific Research. The authors also express their thanks to the Foundation for the Polish Science, which sponsored, within the TECHNE'2001 Programme, the subassemblies of the universal apparatus for glow discharge assisted treatments.

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ZASTOSOWANIE ORGANICZNYCH ZWIĄZKÓW METALI W WYTWARZANIU WARSTW POWIERZCHNIOWYCH METODĄ PAMOCVD

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S t r e s z c z e n i e. Mieszanina gazowa zawierająca tetraizopropoksytan, azot i wodór była wykorzystana w procesie PACVD prowadzonym w temperaturze 500°C do otrzymania warstw Ti(NCO) o wysokiej twardości, odporności na korozję i tarcie. W pracy przedstawiono metodę która pozwala na podwyższenie własności warstw Ti(NCO) i kompozytów warstwa azotowana + Ti(NCO) przez azotowanie plazmowe. Opisano strukturę otrzymanych warstw i określono odporność na korozję i tarcie. Przedstawiono także możliwości otrzymania warstw azotku chromu z mieszanin gazowych zawierających pary acetyloacetonu.

S ł o w a k l u c z o w e : warstwy powierzchniowe, odporność korozyjna, azotowanie plazmowe.